Study of the electrocoagulation of electroplating industry wastewaters charged by nickel (II) and chromium (VI)

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Abstract

The coagulation-flocculation is one of the techniques used for the treatment of industrial wastewaters. In this process, the principle of treatment consists on destabilizing negative colloidal particles, by addition of salts metal cations. The positive charge of cations compresses the electrical double layer which surrounds the colloidal particles characterized by a negative potential (ζ, Zeta Potential). The iron and aluminum salts are the most used. Electrocoagulation is derived from the conventional coagulation technique. The cations are generated in solution by electrolytic dissolution of the metal electrodes. The main advantages of this process, highlighted by several authors, are low dose of coagulant, reduction of salinity, enhanced reactivity of metal cations, oxidation of certain pollutants, compactness of installations, lower volume of sludge, and elimination of the small size colloidal particles. This paper reports a research work on wastewaters eletrocoagulation of an electroplating industry located in Casablanca (Morocco). The goal is to carry out some tests of depollution applying two voltages 6 and 12 V on aluminum electrodes and to evaluate its performance. Abatement rates determined for 6 V reached 57%, 63% and 42%, and 12 V for 77%, 88% and 66%, respectively for Chemical Oxygen Demand (COD), nickel and chromium. The elimination of these pollutants was done by adsorption on aluminum hydroxide or its polymers which were formed in the pH range of this study, but also by the precipitation of nickel (II) and chromium (III) which forms afterward the cathodic reduction of chromium (VI).

Keywords: Electroplating industry, Electro coagulation, Nickel, Chrome, Aluminum hydroxide, Wastewater

Introduction

The wastewater generated from chemical industries contains very harmful pollutants to the environment. To reduce their negative effects, several treatment processes including physicochemical techniques, are implemented viz., adsorption [1], ion exchange [2], precipitation [3], reverse osmosis [4], coagulation.
Electrocoagulation (EC) technique is derived from the coagulation-flocculation. It has been successfully used in the treatment of various emissions : water washing [5], discharges of oil [6], water containing metal ions such as arsenic [7-8], copper, lead, cadmium [9], iron [10,11], chromium [12-14].

1. Theory of electrocoagulation

EC involves several chemical and physicochemical phenomena due to electrolysis. Generally three steps occur in a successive way: (i) formation of coagulants by dissolution of anode (sacrificial electrode), (ii) coagulation of contaminants and particulate suspension and breaking of emulsions and (iii) aggregation of the destabilized by flocuation or adsorption on the metal hydroxide flocs or its polymers.
The colloidal particles forming a stable suspension (negative Zeta Potential ζ) are destabilized by addition of metal cations. The most commonly used metals are iron and aluminum [15] because of their low costs and their high valence (+III). Their positive charge interacts with negative charge of contaminants and compresses their diffuse double layer, and thus reduces the electrostatic interparticle repulsion (negative Zeta Potential ζ) and

even eliminates it. Consequently, coagulation can occur with formation of flocs that entraps and bridges colloidal particles still remaining in the aqueous medium.

EC reactor is fed by a DC generator. The amount of metal electrolyzed is dependent on current supplied by the generator. This amount can be expresses by Faraday's law:

$$m_{theoritical} = \frac{I * t * M}{n * F} \qquad (1)$$

where m is the theoretical quantity of electrode material dissolved in gramme, I the current in Ampere, t the time in sec, M the molar mass of the metal of electrode in gramme, n the number of electrons in oxidation/reduction reaction, F the Faraday's constant, 96,500 Cmol^{-1}.

The theoretical mass calculated by the Faraday's law can be different from the real mass. Indeed, only a part of the overpotential will be used for electrolysis, the rest will be dissipated by Joule effect and used to overcome the overvoltage at both electodes. The applied overpotential is thus written:

$$\eta AP = \eta Mt + \eta k + \eta IR \qquad (2)$$

where ηAP is the applied overpotential, ηMt the concentration overvoltage, ηk the kinetic overpotential *and* ηIR the overpotential caused by solution ohmic drop.

Concentration overpotential, also called the mass transfer or diffusion overvoltage, is due by the concentration gradient near the electrode caused by electrolysis. It can be reduced by eliminating this gradient by increasing the transport of cations from the anode surface to the bulk solution, i. e. by increased mixing between the electrodes.

Kinetic overpotential (also called activation potential) has its origin in the activation energy barrier to electron transfer reactions.

The ohmic drop depends on the following operating parameters: inter-electrode distance, the electrode surface and solution conductivity. Control of these parameters can reduce it. It can be expressed as follows:
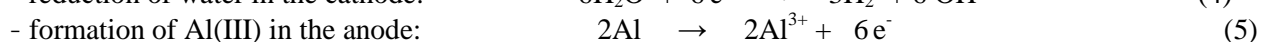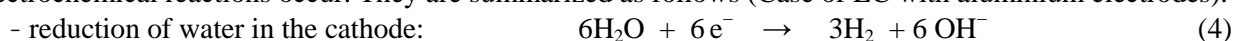
$$\eta IR = \frac{I * d}{A * k} \qquad (3)$$

d: distance between electrodes (cm).
A: active surface of electrode (cm²).
k: solution conductivity (S cm^{-1})
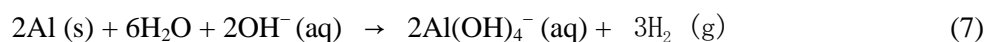
2. Reactions at the electrodes

Electrocoagulation can be made when a potential is applied from external power source to electrodes. In case of a simple electrocoagulating reactor formed by one anode and one cathode (Figure 1), some reactions and electrochemical reactions occur. They are summarized as follows (Case of EC with aluminium electrodes):

- reduction of water in the cathode: $\quad\quad 6H_2O + 6e^- \rightarrow 3H_2 + 6OH^- \qquad (4)$
- formation of Al(III) in the anode: $\quad\quad\quad 2Al \rightarrow 2Al^{3+} + 6e^- \qquad (5)$

When the pH is favorable, these two species can react to form Al(OH)$_3$ according to the following reaction:
$$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3 \qquad (6)$$
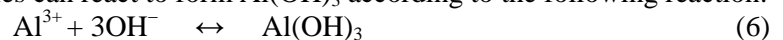
- attack of the cathode for alkaline pH:
$$2Al\,(s) + 6H_2O + 2OH^-\,(aq) \rightarrow 2Al(OH)_4^-\,(aq) + 3H_2\,(g) \qquad (7)$$

- formation of oxygen in the anode and hydrogen in the cathode by electrolyze of water.
$$2H_2O\,(l) \rightarrow 4H^+\,(aq) + O_2 + 4e^- \qquad (8)$$
$$2H_2O\,(l) + 2e^- \rightarrow H_2(g) + 2OH^-\,(aq) \qquad (9)$$
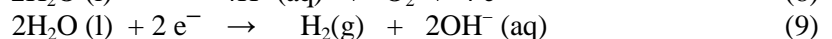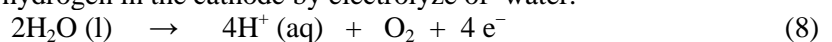
The gases released by the EC contribute to the elimination of a part of the suspended matters by electro flotation (EF). The small size of gas bubbles allows them to join efficiently to the suspended solid material. According to the experimental conditions, the diameter of bubbles was reported to be between: 22 and 50 µm [6], 20 and 70 µm [16], and 10 to 100 µm [17].

According to the pH of the medium, Al^{3+} and OH$^-$ give rise to various hydroxylated cations forms (Figure 2). In acidic medium, the predominance of the free cation Al^{3+} is observed until pH 3.5. As the pH increases, different hydroxo-complexes including monomers and polymers take part in the distribution such as Al(OH)$^{2+}$, Al(OH)$_2^+$, Al$_2$(OH)$_2^{4+}$, Al$_6$(OH)$_{15}^{3+}$, Al$_7$(OH)$_{17}^{4+}$, Al$_8$(OH)$_{20}^{7+}$, Al$_{13}$O$_4$(OH)$_{24}^{7+}$, Al$_{13}$(OH)$_{34}^{5+}$. Between pH 4 and 9, the solid phase consisting of the precipitation of the neutral form Al(OH)$_3$ and its polymerized structures (Reaction (10)) pedometers this pH interval and gives place to some aluminates in basic medium:
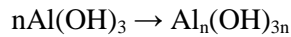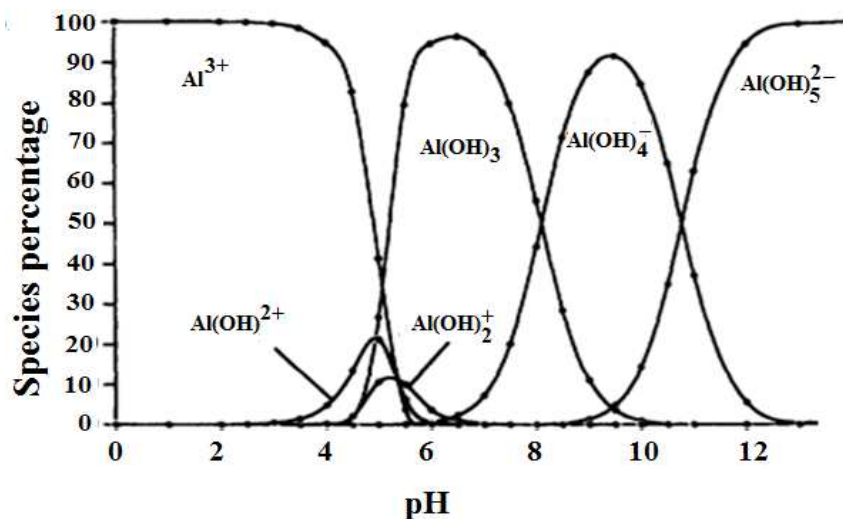
$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \tag{10}$$

The following diagram shows some monomer phases formed by Al^{3+} as a function of the pH.
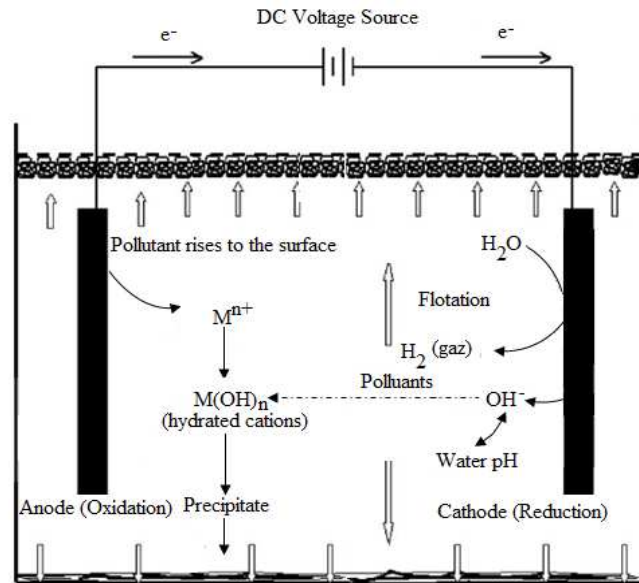
Figure 1: Principle of electrocoagulation [18]

Figure 2: Aluminum hydrolysis species distribution as a function of pH.

Total Concentration in Al^{3+} = 1.85 x10^{-6} mol /L (0.5 mg/L) (Black et Willems, 1961).

Cations released through the EC eliminate a lot of pollutants (Suspended and colloidal matters, dyes, heavy metals) by electrostatic destabilization or by adsorption on the metal hydroxide flocs or its polymers. The main advantages of electrocoagulation process highlighted by several authors [19-20] are the highly chemically reactive M^{n+}, OH^- and superoxide HO_2^- radicals, the compactness of the installations, the lower volume of sludge, the removal of colloidal particles of small size, the induced flotation brings the pollutants to the surface, the cathodic reduction of impurities, the electrophoretic migration of the ions in solution, the reduction of metal ions at the cathode, other electrochemical and chemical processes.

Nevertheless, this technique has some disadvantages:

- High coast, if large consumption of electrodes ;
- electrodes must be replaced regularly;
- need for having electrical energy;
- formation of an oxide film on the cathode, making thus difficult the electronic transfer and thereafter the effectiveness of EC;
- need to have a good conductivity in some discharges cases.

3. Objective of study

The main objective of this study was the monitoring of some physicochemical parameters under 6 and 12V and the evaluation of the direct electric potential effects on the electrocoagulation performances in the treatment of wastewaters charged by heavy metals like nickel and chromium and COD.

4. Materials and methods

The EC experiments were performed on the settled wastewater of electroplating industry with two aluminum electrodes fitted in a volume of 1.8 liters. The electrodes have the following dimensions: length = 15 cm, width = 5 cm, thickness = 6 mm and an active surface of 60 cm^2. The distance between electrodes was 1 cm.

The wastewater was stirred using a magnetic bar, placed in the bottom of the electrolytic cell (Figure 3). This was necessary to ensure a good mix between Al^{3+} and OH^-. The agitation intensity was adjusted to avoid destroying the flocs.

During testing, samples of 20 ml were taken by means of a hose connected to the reactor at intervals of 30 minutes and filtered using Whatman filter paper No.4. The measured parameters were pH, conductivity, COD, concentrations of chromium, nickel and aluminum cations.
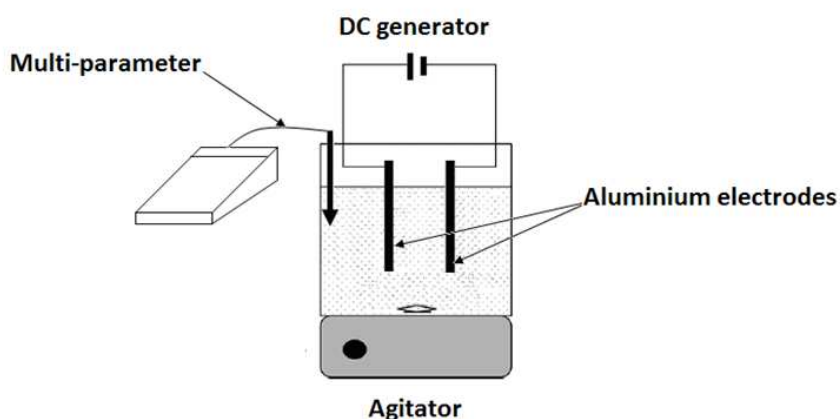
Figure 3: Schematic Diagram of the Experimental reactor used in electrocoagulation

The apparatus used for measuring pH was an Accumet Research AR5 Dual Channel pH/Ion meter pH-meter from Fisher Scientific. This device with a double junction uses an electrode Canlab with internal reference of Ag/AgCl. The calibration was performed using pH buffer solutions 2.00, 4.00, 7.00 and 12.45. Before each measurement the electrodes were cleaned daily with 0.1 M hydrochloric acid solution and immersed in a 3.8 M KCl.

Conductivity was monitored with a conductivity meter Oatkon, pH/conductivity/TDS/°C/°F Meter. It was calibrated before each test with standard solutions. The used electric generator was for direct current type Xantrex XFR 40-70, DC Power supply 0-40 V; 0-70 A. COD was measured according to the 5220 method [21]. Metals (Cr, Ni and Al) were analyzed using inductively coupled plasma spectrophotometry (ICP-AES) with the help of Varian model Vista AX. A 5 % matrix (v/v) concentrated HNO_3 (98 %, reagent ACS) was used for the conservation of samples. To make sure the conformity of the measures quality controls, analysis were realized with certified liquid samples (Standard multi-elements, catalog number 900-Q30-100, SCP Science, Lasalle, Québec). The average wastewater characteristics studied are shown in Table 1.

Table 1: Characteristics of wastewater of electroplating industry

| DCO (mg/l)	Chromium (mg/l)	Nickel (mg/l)	Aluminum (mg/l)	pH	Conductivity (ms/cm)
4940	6,7	16, 30	0,018	8,15	0,52

5. Results and discussions

Figure 4 shows the reactor temperature over time for the two voltages. The temperature increases from 19 to 23°C for 6 V and from 19 to 25°C for 12 V. The increasing due to the electrical energy, was slightly marked for 12 V.

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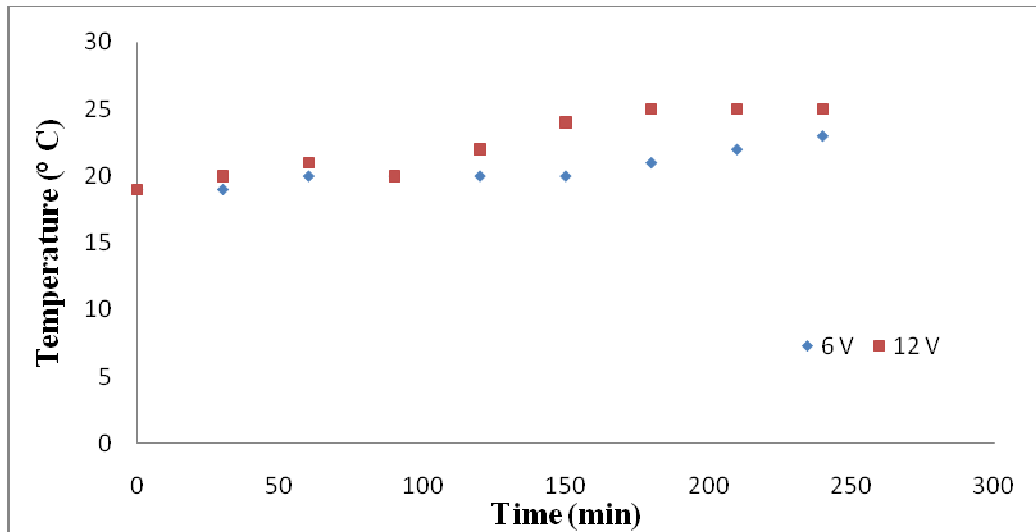
Figure 4: Temperature evolution versus time

The pH of the solution was not fixed during the EC. Figure 5 presents its evolution as a function of the voltage applied to the electrodes and over time.
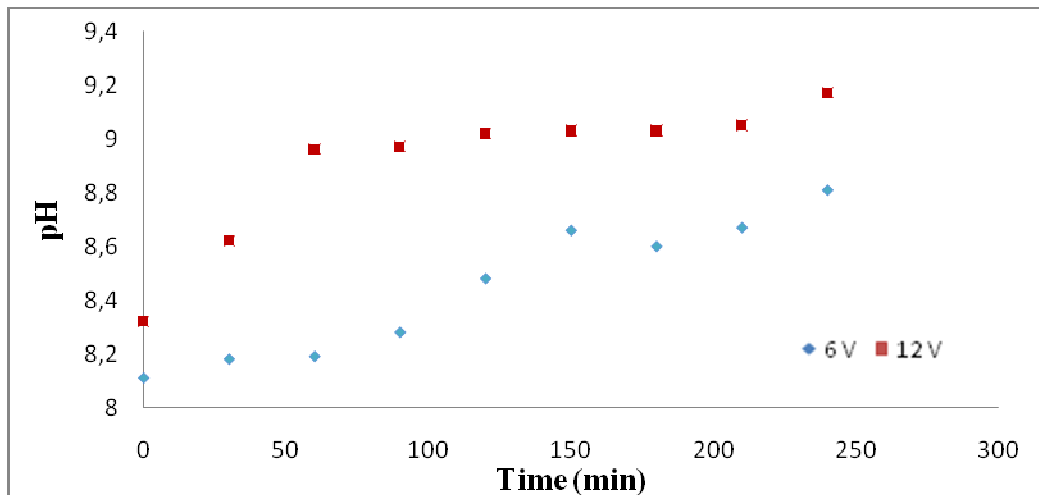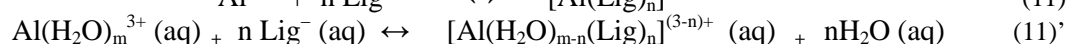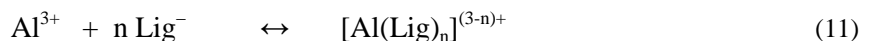

Figure 5: Evolution of the pH as a function of time.

It is well known that the pH plays a significant role in electrocoagulation [22, 23]. Some authors showed that it increases when its initial value was lower than 8, whereas it decreases when its initial value is higher than 8 [24]. In the case of our study, the pH increases although its value was greater than 8. It seems that at this pH precipitation of $Al(OH)_3$ does not occur immediately in a substantial way. It occurs only at the end of 60 minutes under 12 V and 150 minutes under 6 V.

In the same time, the concentration of Al^{3+} ions increased with the potential, and over time to stabilize after 250 minutes (Figure 6), probably corresponding to the precipitation of the aluminum hydroxide.

Late precipitation of $Al(OH)_3$ may be due to:

1) The unavailability of aluminum in cationic forms (or its polynuclear structures) due to the complexation of Al^{3+} by various ligands (Lig^-) present in the wastewater. The reactions taking place are written as follows:

$$Al^{3+} + n\,Lig^- \quad \leftrightarrow \quad [Al(Lig)_n]^{(3-n)+} \tag{11}$$

$$Al(H_2O)_m{}^{3+} (aq) + n\,Lig^- (aq) \leftrightarrow [Al(H_2O)_{m-n}(Lig)_n]^{(3-n)+} (aq) + nH_2O (aq) \tag{11'}$$
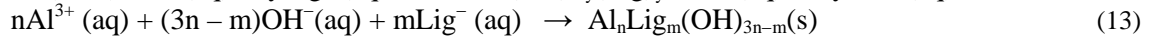
These ligands can be anions like chlorides, nitrates, sulfates, organic molecules containing functional groups as hydroxyl, phenol, carboxyl, [25] and colloids.

Many authors have shown the important role played by the ligands during the coagulation [20, 26-27]. Their presence leads to the sequestration of Al^{3+}, but at the same time can promote the treatment of water by neutralization, sweep coagulation or by adsorption according to the pH of the medium [28].

2) The formation of mononuclear and/or polynuclear aluminum structures (Reaction (10)) involving anions

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and generating several reactions of formation or dissociation structures is pH dependant [20]. Although the hydroxide ions had a great affinity for Al^{3+} that can be substituted by some anions according to their concentrations (Reaction (12)) such as sulfates, chlorides, present in the discharge [20,29], co-precipitation can also occur according to the reaction (13) [30]:

$$Al(OH^-)_x^{(3-x)+} \text{ (aq) } {}_+ \text{ } yLig^- \text{ (aq) } \leftrightarrow \text{ } [Al(OH)_{x-y}(Lig)_y]^{(3-x)+} \text{ (aq) } {}_+ \text{ } yOH^- \text{ (aq)} \tag{12}$$

$$nAl^{3+} \text{ (aq) } + (3n-m)OH^- \text{(aq)} + mLig^- \text{ (aq) } \rightarrow Al_nLig_m(OH)_{3n-m}(s) \tag{13}$$
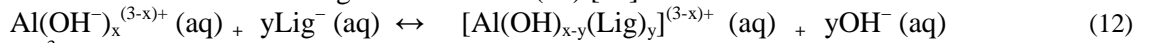
3) The formation of aluminates $Al(OH)_4^-$ which is considered as the precursor of Al_{13} polymer [31, 32] by alkaline attack of the cathode (Reaction (7)) or by reaction (14) between $Al(OH)_3$ and OH^-, is favored in the pH range 8-10 [33].
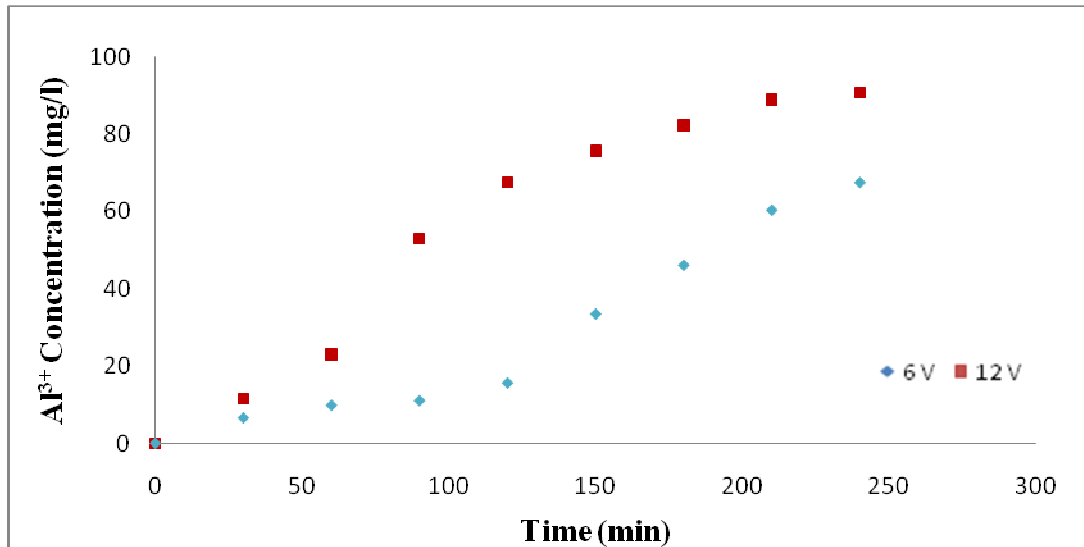
$$Al(OH)_3 \text{ } + \text{ } OH^- \text{ } \leftrightarrow \text{ } Al(OH)_4^- \tag{14}$$
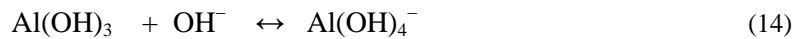
Figure 6: Al^{3+} concentration in wastewater versus time

Figure 7 relates to the residual concentrations respectively of chromium (VI) and nickel (II). They decreased over time and with the voltage applied to the electrodes.
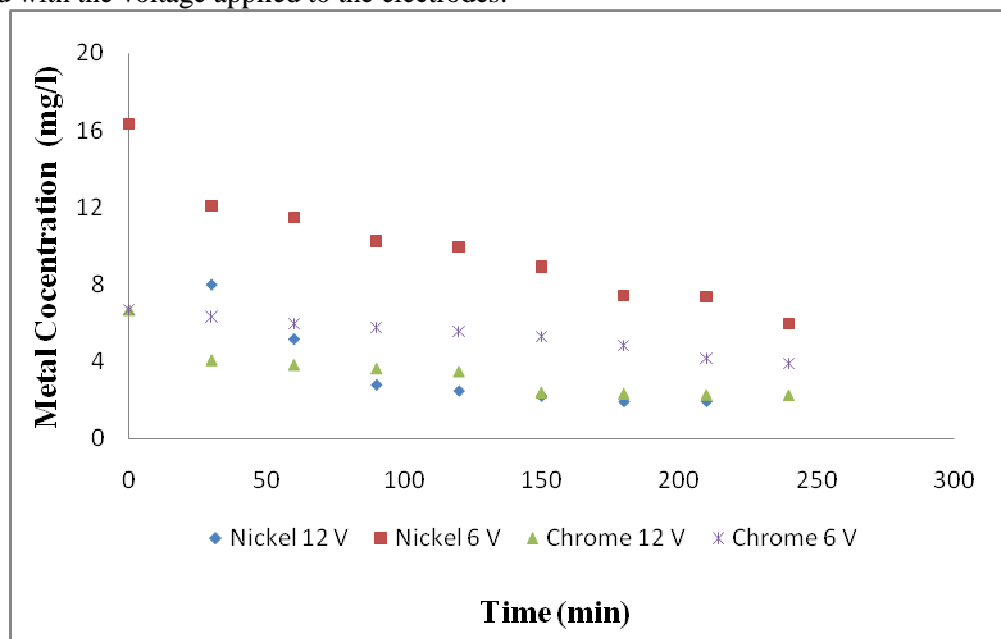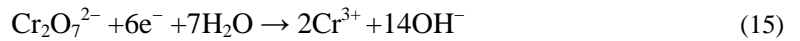

Figure 7: Evolution of residual concentrations of chromium (VI) and nickel (II) versus time

In the EC, heavy metals may react in different ways. They can undergo:
• a reduction at the cathode, as in the case of chromium (VI):

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$$Cr_2O_7^{2-} + 6e^- + 7H_2O \rightarrow 2Cr^{3+} + 14OH^- \tag{15}$$

- or oxidation, as in the case of iron:

$$Fe^{2+} \rightarrow Fe^{3+} \tag{16}$$

- or precipitation of the metals according to the following reaction:

$$M^{n+} + n(OH)^- \leftrightarrow M(OH)_n \downarrow \tag{17}$$

The favorable range of pH for the precipitation of nickel is between 4 and 9 as reported by some authors [6, 34]. The same authors showed, on the other hand, that the residual concentration of chromium increases when the pH becomes higher than 8.

The results found in these tests were in conformity with those published by other authors [34-36]. This study showed that the pH interval (8.11-9.17) promote the elimination of nickel by precipitation. The metal removal can also be done by adsorption on flocs of $Al(OH)_3$ or its polymers.

Concerning chromium, its removal can also be done either by precipitation following its cathodic reduction (Reaction (15)), or by adsorption as chromium (III) or chromium (VI) on the aluminum hydroxide or its polymers. Indeed, Gao et al (2004) [37] have shown that electrocoagulation using iron electrodes allowed to remove chromium (VI) with a good performance in the pH range 6-8. This elimination was improved with the addition of Al^{3+}, probably by adsorption on the floc of $Al(OH)_3$ formed.

Figure 7 shows that the rate of reduction of nickel was better than chromium. The removal efficiencies were reported in Table II. The difference between metals abatement is probably, due to precipitation rather than elimination by adsorption. On the other hand, reduction of chromium (VI) does not occur significantly.

Table 2: Removal efficiency of the nickel and chromium according to the applied voltage after 210 min of EC

	6 V	**12 V**
Nickel (II)	54,9	88,22
Chromium (VI)	38,41	65,79

The abatement of the COD (Figure 8) was done very slowly, due to the late precipitation of $Al(OH)_3$ as explained above. Final yields reached 57% and 77% respectively at 6 V and 12 V for a period of 4 hours. Given the initial concentration of the rejection (4940 mg/l), the residual COD remain relatively high. The difference in yield was related to the concentration of $Al(OH)_3$ which precipitates more easily at 12 V than 6 V. This allowed to absorb more elements responsible of COD like fine colloids and soluble organic matter [6].
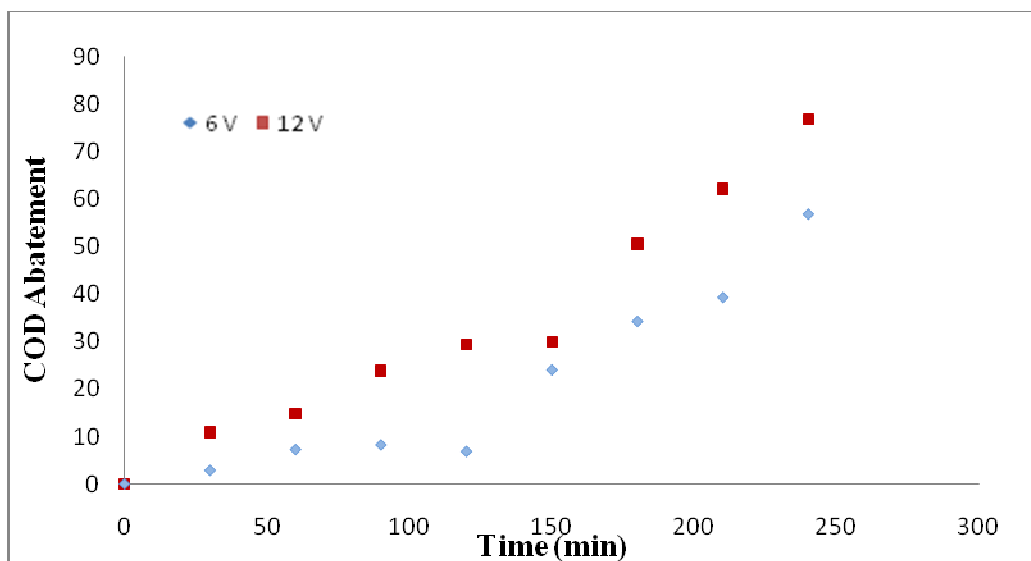
Figure 8: COD evolution versus time

Examination of figure 9 shows that the conductivity decreases slightly when the voltage increases over time [38]. This can be attributed to:

- the reduction in the concentration of negative ions, which combine to Al^{3+}, according to the reaction (11);
- the polymer formation according to the reaction (10);
- the adsorption of positive ions, on the flocs of aluminum hydroxide or on its polymers;
- the formation of structures of very low mobility in alkaline medium like $Al(OH)_4^-$ formed from reactions (7) (14), (15) and $Al(OH)_5^=$ formed from reaction (18).

$$Al(OH)_4^- + OH^- \leftrightarrow Al(OH)_5^= \quad (18)$$
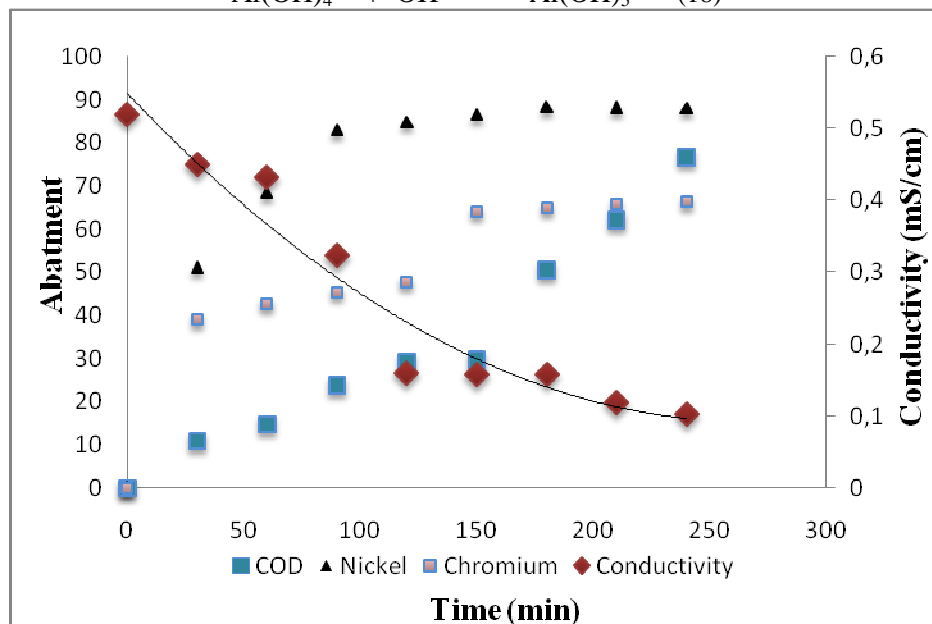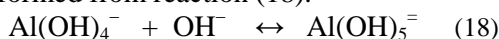
Figure 9: Conductivity versus time

Several authors have shown that the conductivity was a favorable parameter of electrocoagulation. It allows the ions transport and therefore, reduce the pollution [39-40]. But in our case, the relation between conductivity and abatement was not normal. One notes increasing of abatement of all parameters (chromium, nickel and COD) when conductivity decreases (Figure 9). The ions transport was limited and not favorable for EC. It seems that elimination of physicochemical parameters occurs not only by electrochemical process but also by chemical reactions that occurs in cathode (Reaction (7)). The formation in situ of $Al(OH)_3$ allowed discharge treatment and contribute to eliminate the pollutants.

Conclusions

The technique of electrocoagulation used to eliminate the pollutants of the electroplating pollution gave convincing results. Indeed, this study has highlighted a number of conclusions:

1) despite that the initial pH of the solution was greater than 8, the precipitation of $Al(OH)_3$ doesn't occur immediately;
2) the concentration of Al^{3+} ions increases with time at the beginning and stabilizes. This was probably due to the presence of negative ligands acting as a competitor of OH^- for the Al^{3+} cations;
3) the conductivity decreases slightly when the potential between electrodes increases as it decreases as a function of time for a given tension. Formation of Al^{3+} complexes, polymerization of the $Al(OH)_3$, adsorption of ions on the aluminum hydroxide and its polymers and formation of structures of low mobility such as $Al(OH)_4^-$ and $Al(OH)_5^=$ which formed in basic medium, are the main reasons which explain the decreasing of conductivity;
4) the diminution of conductivity does not promote the transport of ions, therefore the formation of aluminum hydroxide, which adsorb pollution agents do not play its entire role. Furthermore, the decrease of conductivity was not able to explain the rates of physiochemical parameters abatements. These abatements were probably due to the chemical reaction occurring between metal and hydroxide ions resulting from water reduction at the cathode.

In addition, the rates of abatement determined in these tests reached 57%, 63% and 42% for 6 V, and 77%, 88% and 66% for 12 V, respectively for the colloidal COD, nickel and chromium. The elimination of the various compounds was done by adsorption on the aluminum hydroxide or its polymers, which were formed in the interval of pH of this study, but also by precipitation of nickel II and chromium (III). This latter is formed through the cathodic reduction of chromium (VI).

The abatement of nickel was more marked because the pH was favorable to its elimination. This was not the case for

chromium since thermodynamic conditions do not lead to an efficient elimination in this pH field. More especially its probable complexation by the organic matter would slow down its precipitation.

The abatement of the COD was a slow process which depends on the pH of the medium. The quantity of $Al(OH)_3$ which constitutes the matrix of adsorption was not sufficient to eliminate all the COD, because its limited formation in presence of some ligands. In addition, the pH of the medium becoming basic solubilized the aluminum hydroxide in the form of aluminates, which makes $Al(OH)_3$ unavailable for the adsorption of the COD.

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